Iodine Adsorption in a Redox-Active Metal–Organic Framework: Electrical Conductivity Induced by Host–Guest Charge-Transfer

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Supporting Information

ABSTRACT: We report a comparative study of the binding of I₂ (iodine) in a pair of redox-active metal–organic framework (MOF) materials, MFM-300(VIII) and its oxidized, deprotonated analogue, MFM-300(V IV). Adsorption of I₂ in MFM-300(VIII) triggers a host-to-guest charge-transfer, accompanied by a partial (∼30%) oxidation of the V III centers in the host framework and formation of I3⁻ species residing in the MOF channels. Importantly, this charge-transfer induces a significant enhancement in the electrical conductivity (Δσ = 700 000) of I₂@MFM-300(V III/IV) in comparison to MFM-300(V III). In contrast, no host–guest charge-transfer or apparent change in the conductivity was observed upon adsorption of I₂ in MFM-300(V IV). High-resolution synchrotron X-ray diffraction of I₂@MFM-300(V III/IV) confirms the first example of self-aggregation of adsorbed iodine species (I₂ and I3⁻) in three infinite helical chains within a MOF.

INTRODUCTION

Nuclear energy shows promise to bridge future gaps in the supply of electricity. However, the radionuclides generated from the nuclear power plant can pose significant risks on both human health and ecosystems if emitted into the environment. Radioactive iodine (primarily comprised of 129I and 131I) is a key volatile waste that can be spread through air and interfere with human metabolic processes. Various techniques and materials have been applied for I₂ capture, and porous materials, because of their high porosity and fast adsorption kinetics, are considered to be emerging sorbents for the efficient removal of I₂.

Porous solid-state sorbents with rigid structures such as zeolites, C atoms, and silica materials have been widely studied for I₂ adsorption. Metal–organic framework (MOF) materials provide a unique platform to investigate their interaction with adsorbed I₂ because of their crystalline nature and tunable structural properties. Various approaches, including linker functionalization and shaping of the porosity, have been reported to improve I₂ adsorption in modified MOFs. However, the binding of I₂ in MOFs with redox-active metal centers (e.g., FeII/III, CrII/III, V III/IV, and NiII/III) remain largely unexplored, which can be attributed to the scarcity of reported stable redox-active MOFs. Furthermore, collapse or, to a lesser extent, degradation of the MOF upon inclusion of I₂ can occur, thus restricting the investigation of the host–guest binding via a charge-transfer mechanism.

Herein we report the adsorption and structural study of binding domains for I₂ in a pair of stable redox-active MOFs, MFM-300(VIII) and MFM-300(V IV). Host–guest charge-transfer has been unambiguously observed in MFM-300(VIII) by electron paramagnetic resonance (EPR) spectroscopy, promoting a 70 000 times enhancement in the electrical conductivity of the I₂-loaded MOF material in comparison to MFM-300(VIII). In contrast, there is an absence of host–guest charge-transfer or an apparent change in the conductivity for

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I₂-adsorbed MFM-300(VIV). We also report the unusual self-aggregation of confined I₂ and I⁻⁻ molecules into a 1D helical chain within the channels of MFM-300(V).

RESULTS AND DISCUSSION

Structure of MFM-300(VIII/IV). MFM-300(VIII/IV), [V₂(OH)₂(L)] (H₄L = diphenyl-3,3',5,5'-tetracarboxylic acid), crystallizes in a tetragonal system in which the V III center is coordinated by six O donors, four from carboxylates and two from bridging hydroxyl groups μ₂-OH. This affords an infinite chain of [V₂(OH)₂O₄] moieties along the c axis (Figure 1), and these are further bridged by the deprotonated organic linkers to afford rigid wine-rack-type open framework with square-shaped channels of ~6.7 Å diameter. Oxidation of MFM-300(VIII) in air yields the analogue MFM-300(VIV), [V₂(O)₂(L)], where the V III center is oxidized to V IV, and this is coupled with deprotonation of hydroxyl to oxygen bridges. MFM-300(VIV) retains the same overall framework topology except for a small contraction on the V–O bond distances accompanied by a slight decrease in the pore volume from 0.49 to 0.48 cm³ g⁻¹ upon oxidation.

Iodine Adsorption in MFM-300(VIII/IV). The as-synthesized MOFs were exchanged with acetone over a period of 1 week. The desolvated samples were prepared by heating the acetone-exchanged samples under vacuum at 150 °C until no weight loss of solvent was observed by thermogravimetric analysis (TGA). The desolvated MOF was transferred into a vessel under dry N₂ containing a vial of solid I₂. The I₂ use into the desolvated MOF at 343 K for 2 days to allow full adsorption. The color of both MOF materials is fully reversible, and no apparent loss in capacity was observed for three cycles of sorption–desorption in both MOFs (Figures S4–S6). The densities of adsorbed I₂ within the pores of MFM-300(VIII) and MFM-300(VIV) are calculated to be 2.90 and 2.60 g cm⁻³, respectively. The former is comparable to the best-behaving MOF to date [3.08 g cm⁻³ in MFM-300(Sc)].

Determination of I₂ Binding Sites within MFM-300(VIII/IV). The binding sites for adsorbed I₂ molecules within MFM-300(V) have been elucidated by high-resolution synchrotron powder X-ray diffraction (PXRD). Structural analysis of I₂-loaded MOF samples at approximately 1.0 I₂/V loading via Rietveld refinement confirmed the absence of any structural phase changes and revealed formulae of [V₂(OH)₂(L)]·0.6I₂ and [V₂(O)₂(L)]·2.2I₂ for I₂-loaded MFM-300(VIII) and MFM-300(VIV), respectively. Upon loading of I₂ into MFM-300(VIII), changes are observed in the V–O bond lengths and angles, and three independent sites for neutral I₂ molecules and one site for anionic I⁻⁻ are observed within the channel (Figure 3a). Bond-valence-sum (BVS) calculations (Table 1) give an overall valence of 3.28 for the V center, consistent with its partial oxidation, and this is balanced by the presence of triiodide I⁻⁻ anions. The I⁻⁻ anion (occupancy = 0.3) is located near the hydroxyl group from the [V₂(O)₂(OH)₂] moiety with a short distance [I⁻⁻···H–O = 2.94(1) Å], indicating the formation of a strong hydrogen bond between the triiodide and the –OH groups. It is worth noting that protons on the hydroxyl groups cannot be conclusively located from the PXRD data, and it is likely that these protons are partially delocalized to accompany the host–guest charge-transfer. I⁻⁻ is located interstitially between two phenyl rings of neighboring ligand molecules [I⁻⁻·phenyl ring = 4.68(1) and 5.15(1) Å] with an occupancy of 0.25, I₂⁻⁻ and I₂⁻ adopt low occupancies (0.16 and 0.10, respectively), reside in the center of the channel, and are stabilized by intermolecular interactions (Figure S10). These results confirm partial oxidation of the framework by adsorbed I₂ molecules to afford a mixed-valence I₂@MFM-300(VIII/IV) material.

![Figure 1. Views along the b axis of the infinite metal chains in (a) MFM-300(VIII) and (b) MFM-300(VIV). The hydroxyl groups (H atom, white; O atom, red) in MFM-300(VIV) are deprotonated to an O⁻⁻ bridge (red) in MFM-300(VIV).](image1)

![Figure 2. TGA–MS plots for I₂-saturated MFM-300(VIII) and MFM-300(VIV).](image2)
A detailed examination of [V₂(O)₂(L)]·2.2I₂ confirmed that the confined I₂ molecules within the pores aggregate to form an unusual helical chain running through the channel with a distance of 3.51(4) Å between adjacent I₂ molecules. This intermolecular I₂···I₂ distance is comparable to that [3.35(9) Å] observed in the single helical chain of I₂ and I₃⁻ in I₂@MFM-300(VIII/IV) (Figure 3). A more detailed structural analysis of I₂@MFM-300(VIII/IV) by single-crystal X-ray diffraction reveals a similar structural model of infinite helical I₂ chains with an intermolecular I₂···I₂ distance of 3.53(4) Å (Figure S13). To date, the existence of one-fold helical chains of I₂ has only been confirmed by theoretical studies, while the linear I₁ chain has been observed crystallographically in Ln₂Cu₅(OH)₂(H₂pydc)₆(H₂O)₈ (H₂pydc = pyridine-2,5-dicarboxylic acid). Thus, the helical I₂ chain observed in I₂@MFM-300(V) at crystallographic resolution represents the first example of such a motif in porous materials. The formation of triple-helical I₁ chains has been previously observed in MFM-300(SCe).

Spectroscopic Analysis of I₂@MFM-300(VIII/IV). X-ray photoelectron spectroscopy (XPS) was used to investigate the valence of adsorbed I₂ species within MFM-300(V) (Figure 4a,b). For I₂@MFM-300(VIV), one chemical species (one doublet for the spin–orbit splitting of the 3d level) of I₂ was observed with the I 3d₅/₂ photopiton peak at 620.7 eV, indicating that only one type of adsorbed I₂ species is trapped inside the pore and all of the adsorbed I₂ molecules remain neutral. For I₂@MFM-300(VIII/IV), however, two characteristic chemical species (I 3d₅/₂ at 619.1 and 620.7 eV) were observed, corresponding to the I₁⁻ and I₂ moieties, respectively, consistent with the structural models. Electron-accepting guest inclusion results in an increase in the electrical conductivity so measurements of the electrical conductivity of the bare and I₂-loaded MFM-300(V) materials were performed to examine the effect of host–guest charge-transfer.

The conductivity of MFM-300(VIII) was measured to be 1.7 × 10⁻¹⁰ S/cm, but I₂@MFM-300(VIII/IV) shows a significant enhancement (Δσ = 700000) in conductivity in the dark to 1.2 × 10⁻⁴ S/cm (Figure S14). This can be attributed to both the oxidized V−O(H)−V skeletons and generated iodide chains that provide further transport pathways to facilitate electron transfer. The value is comparable to the state-of-the-art conductivity observed for I₂@Cu[Ni(pdt)₂]₁₄ and 2.16 × 10⁻⁴ S/cm for I₂@[Tb₃(Cu₄I₄)₃(ina)₉] (H₂pdt = pyrazine-2,3-dithiol; Hina = isonicotinic acid) (Table 2). Measurements on MFM-300(VIII) and I₂@MFM-300(VIV) show very low conductivities (<1 × 10⁻¹⁰ S/cm) in both cases. Thus, the

Table 1. Bond-Length and BVS Calculations of MFM-300(VIII), MFM-300(VIV), and I₂@MFM-300(VIII/IV)

<table>
<thead>
<tr>
<th></th>
<th>MFM-300(VIII)</th>
<th>MFM-300(VIV)</th>
<th>I₂@MFM-300(VIII/IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V−Obridging (Å)</td>
<td>1.978(1)</td>
<td>1.838(1)</td>
<td>1.901(2)</td>
</tr>
<tr>
<td>V−Ocarboxyl (Å)</td>
<td>2.004(2)</td>
<td>1.971(2)</td>
<td>2.014(1)</td>
</tr>
<tr>
<td>∠V−Obridging−V(O)</td>
<td>125.6(1)</td>
<td>134.7(2)</td>
<td>130.1(1)</td>
</tr>
<tr>
<td>V−V distance (Å)</td>
<td>3.519</td>
<td>3.392</td>
<td>3.447</td>
</tr>
<tr>
<td>BVS calculation</td>
<td>3.027</td>
<td>3.960</td>
<td>3.278</td>
</tr>
</tbody>
</table>

Figure 3. Views along the b axis of I₂-loaded (a) MFM-300(VIII) and (b) MFM-300(VIV) obtained by high-resolution synchrotron PXRD. Views of binding sites for I₃⁻ and I₂ in (c) MFM-300(VIII) and (d) MFM-300(VIV), respectively. Views of I₂ (solid) and I₁⁻ (pale wire frame) in (e) I₂@MFM-300(VIII/IV) and (f) I₂@MFM-300(VIV).

Figure 4. XPS spectra of I₂-loaded (a) MFM-300(VIII) and (b) MFM-300(VIV). EPR spectra of desolvated and I₂-loaded (c) MFM-300(VIII) and (d) MFM-300(VIV). Raman spectra of desolvated and I₂-loaded (e) MFM-300(VIII) and (f) MFM-300(VIV).
Table 2. Summary of Electrical Conductivities for I2-Loaded MOFs

<table>
<thead>
<tr>
<th>MOF</th>
<th>conductivity for bare MOFs (S/cm)</th>
<th>conductivity for I2-loaded MOFs (S/cm)</th>
<th>conductivity enhancement (magnitudes)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu[Ni(pdt)]2</td>
<td>1 × 10^{-4}</td>
<td>1 × 10^{-4}</td>
<td>~10^0</td>
<td>14</td>
</tr>
<tr>
<td>[Cu2(pybz)2(μ-OH)]2(1')</td>
<td>8.04 × 10^{-9}</td>
<td>8.11 × 10^{-7}</td>
<td>~10^2</td>
<td>29</td>
</tr>
<tr>
<td>[Co3(μ-bdc)4(μ2-bpz)]2</td>
<td>2.59 × 10^{-9}</td>
<td>1.56 × 10^{-8}</td>
<td>~10^3</td>
<td>30</td>
</tr>
<tr>
<td>[Co(ebic)]2</td>
<td>2.46 × 10^{-9}</td>
<td>2.21 × 10^{-7}</td>
<td>~10^2</td>
<td>31</td>
</tr>
<tr>
<td>[Eu(μ-L)]3</td>
<td>8.27 × 10^{-7}</td>
<td>2.71 × 10^{-3}</td>
<td>~10^2</td>
<td>32</td>
</tr>
<tr>
<td>IFMC-15</td>
<td>2.59 × 10^{-9}</td>
<td>2.07 × 10^{-7}</td>
<td>~10^2</td>
<td>33</td>
</tr>
<tr>
<td>[(Me,NH2)2][Cd3(5-</td>
<td>1.71 × 10^{-8}</td>
<td>1.30 × 10^{-6}</td>
<td>~10^2</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>tbbp)3]2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MET-3</td>
<td>0.77 × 10^{-4}</td>
<td>1 × 10^{-3}</td>
<td>~10^1</td>
<td>35</td>
</tr>
<tr>
<td>[Tb3(Cu4I4)3(ina)9</td>
<td>5.72 × 10^{-11}</td>
<td>2.16 × 10^{-4}</td>
<td>~10^4</td>
<td>27</td>
</tr>
<tr>
<td>[Zn3(ou-lac),(μ2 prybz)]2</td>
<td>3.47 × 10^{-7}</td>
<td>1.16 × 10^{-10}</td>
<td>~10^6</td>
<td>this work</td>
</tr>
<tr>
<td>[Zn(ebic)]2</td>
<td>4.33 × 10^{-9}</td>
<td>3.47 × 10^{-7}</td>
<td>~10^2</td>
<td>31</td>
</tr>
<tr>
<td>MFM-300(VIII)</td>
<td>1.7 × 10^{-10}</td>
<td>1.16 × 10^{-4}</td>
<td>~10^6</td>
<td>this work</td>
</tr>
</tbody>
</table>

The values of the electrical conductivity for solid I2 is 1 × 10^{-9} S/cm. H3pdt = pyrazine-2,3-dithiol, Hpybz = 4-pyridylbenzoic acid, H2bdc = benzene-1,4-dicarboxylic acid, bpz = 3,5,5'-tetramethyl-4,4'-bipyrrozole, Hedic = 2-ethyl-1H-benzo[d]imidazole-5-carboxylic acid, H2L1 = biphenyl-3,4',5-tricarboxylate, H2-5-tbip = 5-tetraethyl-5-carboxylic acid. Hina = isonicotinic acid, H2-DL-lac = lactic acid, Hpybz = 4-pyridylbenzoic acid, and Hedic = 2-ethyl-1H-benzo[d]imidazole-5-carboxylic acid. Films were used for testing of the electrical conductivity. Single crystals were used for testing of the electrical conductivity.

**CONCLUSION**

In summary, we report the adsorption and binding domains of I2 in a pair of redox-active MOF materials, MFM-300(VIII) and MFM-300(VIV), which provide an excellent platform to examine the host–guest charge-transfer properties. Adsorption of I2 in MFM-300(VIII) induces host–guest charge-transfer via partial oxidation of the V centers and formation of I3- species in the pore to balance the overall charge. As a result, 7 × 105 enhancement of the electrical conductivity is observed for the I2-loaded mixed-valence I2@MFM-300(VIII/IV). In contrast, there is an absence of host–guest charge-transfer observed for MFM-300(VIV) upon loading of I2 with no change in the inherent low conductivity of the parent MOF. In both cases, unusual self-aggregation of confined I2 molecules into helical chains within the MOF hosts has been observed at crystallographic resolution, defining the molecular details for the underlying host–guest binding interactions and paving the way for the design and discovery of new functional materials with improved I2 adsorption properties.

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b02176.

Synthesis, iodine adsorption measurements, powder X-ray diffraction, SEM images, and Rietveld refinement results (PDF)

Accession Codes

CCDC 1915136–1915138 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Chemically and Mechanically Robust Zr and Hf MOFs.


Yin, Z.; Wang, Q. X.; Zeng, M. H. Iodine Release and Recovery, Influence of Polypodide Anions on Electrical Conductivity and


